Effect of Electrolyte on Adsorption of Dye at Clay – water Interface

Thesis submitted

By

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National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, **"EFFECT OF ELECTROLYTE ON ADSORPTION OF DYE AT CLAY – WATER INTERFACE"** submitted by Ankit Kedia in partial fulfillments for the requirements for the award of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any Degree or Diploma.

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Abstract

Presence of color impurity as an effluent poses a significant risk to the environment and human health. Industrial effluents mostly go untreated into the water streams and render it unfit for the use. Existing methods for effluent treatment such as charcoal adsorption are less effective, costly and less ecological friendly in nature. In the present work, kaolinite has been used as an adsorbent, with different electrolytes (Na_2SO_4, NaCl, and CaCl2) as adsorption enhancers. Kaolinite clay is easily available and also eco-friendly in nature, with a good adsorption property. Different batches of methylene blue and kaolinite clay has been studied and further adsorption enhancement of adsorption by the salts has been carried out. Addition of salt such as Na_2SO_4 led to a 100% increment in the adsorption capacity of the clay.

Keywords: Adsorption, Surfactants, Clay, Salts

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Chapter 1

Introduction

INTRODUCTION

Adsorption refers the adhesion of the atoms of ions or molecules from gas, liquid or dissolved solid to a surface. There are two terminologies related to this observation: Adsorbent and Adsorbate. A layer of adsorbate generally forms on the surface of the adsorbing substance or adsorbent. The process occurs as a consequence of the surface energy of the adsorbent and adsorbate. Adsorption can be of two types depending on the type of species involved. The process is classified as physisorption when forces are weak Van der Waals in nature and it is chemisorption if the bonding is covalent in nature.

1.1 Surface Tension

The property results from the cohesion of similar type of molecules coming together and creating a contractive tendency of the surface of the liquid thus allowing it to resist an external force. It has the dimension of force per unit length or of energy per unit area.

1.2 Double Layer

The layer refers to the formation of two parallel layers of charge surrounding the object. Of these, the first layer comprises of the ions directly adsorbed onto the object. The second layer comprises of the ions attracted to the surface charge via the Coulomb force, electrically screening the first layer.

1.3 Salt

Ionic compound formed as a result of the neutralization reaction of an acid with a base. It consists of equal number of charges (Cation and Anion) and thus, the product is electrically neutral.

1.4 Solubility

It is the formation of a homogeneous solution of the solute in the solvent by dissolution of a solid, liquid or gaseous solute in a solid, liquid or gaseous solvent. Solubility can depend on many factors such as temperature, pH of the solvent, solute concentration. The final solution formed may or may not have the same properties as that of the solvent taken.

1.5 Spectroscopy

The term is used to measure the radiation intensity as a function of wavelength. Spectroscopic data is often represented by a spectrum, a plot of the response of the interest as a function of wavelength or frequency. UV spectroscopy considers absorption spectroscopy or reflectance spectroscopy in the ultraviolet- visible spectral region.

1.6 Centrifugation

It is mainly used to separate solvent from solute particles. The separation is achieved by making use of centrifugal force for the centrifugation of mixture. The rate of centrifugation is specified by the angular velocity measured in revolutions per minute (RPM).

1.6.1 Microcentrifuges

They are mainly used to operate for small volume samples of cells, biological molecules or nuclei. The tube holding capacity is around 0.5 – 2mL of liquid and are spun at maximum angular speed of 12000 – 13000rpm.

1.6.2 High-speed centrifuges

They have capacity to operate even for larger volume of samples, from few tens to as high as several litres. They rotate at around 30000rpm at their maximum speed of rotation.

1.6.3 Ultracentrifuges

They are mainly used when properties of biological particles are needed to be studied. They have the advantage of separating much smaller particles, which is not the case with microcentrifuges and high-speed centrifuges.

Chapter 2

Literature Review

2.1 Introduction

Dye effluents from the dye consuming and manufacturing industries such as paper, food, textile, etc. are one of the most problematic water pollution cases. Also, most of the dyes aren't biodegradable and release of the effluent to the aquatic medium increases the biological load. Discharge of these effluents in the environment leads to some serious health problems as some of these dyes are carcinogenic in nature and affect the living organism's life. Dyes on surface water also acts as a barrier to the penetration of sun light and aeration of water body, and thus also leads to the reduction of photosynthesis activity. The toxic nature of the dye effluents also causes death of soil microorganisms, which are used for irrigation purposes and thus, also affects the productivity of agriculture.

Coloring makes use of Methylene Blue (Cationic) very extensively. It is generally used for drying wool, silk and cotton materials. Any contact of the dye is harmful to the body. MB can cause eye burns in humans and animals, methemoglobinemia, cyanosis, convulsions, tachycardia, irritation to the skin, and if ingested, irritation to the gastrointestinal tract, nausea, vomiting, and diarrhea.

Therefore, decolorization of dye is an important aspect of wastewater treatment before discharge. Removal of dyes from effluent is difficult as they are not biodegradable and are generally not removed from wastewater by conventional wastewater systems. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those that are not easily biodegradable. Currently, a combination of biological treatment and adsorption on activated carbon is becoming more common for removal of dyes from wastewater. Although commercial activated carbon is preferred sorbent for color removal, its widespread use is restricted due to high cost. As such, alternative non-conventional sorbents have been investigated. Therefore, dye removal has been studied in the present work, making use of clay (Kaolinite) as the adsorbing material in presence of different salts, which help in the adsorption enhancement and thus, improves the overall process efficiency.

2.2 Studies on dye removal techniques

Adsorption of dye by different adsorbents has been studied in the past. Baybars et al (2012) studied the removal of Cationic dye (Methylene Blue) from the aqueous solution by making use of Montmorillonite. They made use of batch equilibrium technique and studied the effect of contact time on the amount of dye adsorbed as a function of initial concentration of dye, pH, ionic strength and temperature. Montmorillonite is a phyllosilicate group of mineral, with good adsorption capacity.

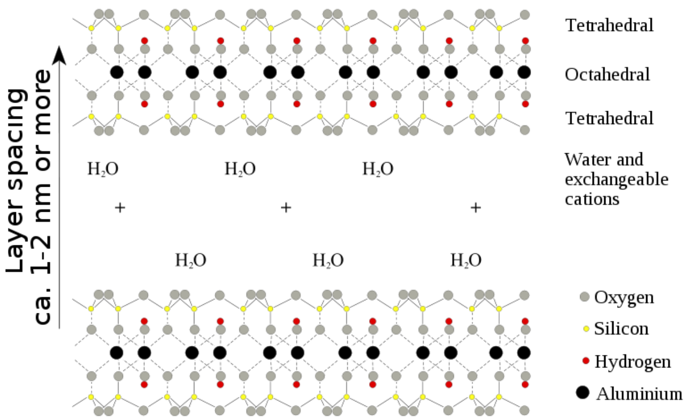

Fig. 2.1 Montmorillonite structure

The results suggested that with the increase in pH, adsorption capacity of Montmorillonite for Methylene Blue increased. However, the same was found to decrease with increased ionic strength and temperature.

Iqbal et al (2006) studied the use of activated charcoal as an adsorbent for dyes from aqueous solutions. Charcoal supplied by the Scientific and Technological Development Corporation of Pakistan (STEDEC) was used for the process. Dyes such as methylene blue (82%, Fluka), methyl violet (85%, Fluka), alizarine Red S (70%, Fluka) and malachite green oxalate (90%, Merk) were used as adsorbates to study the adsorption process. Charcoal provides a high surface area with its much ingrained porosity, which further acts as a contributing factor for the adsorption. Based on the varying of parameters such as Time optimization and Optimization of amount of adsorbent, the results were analyzed for the different dyes used.

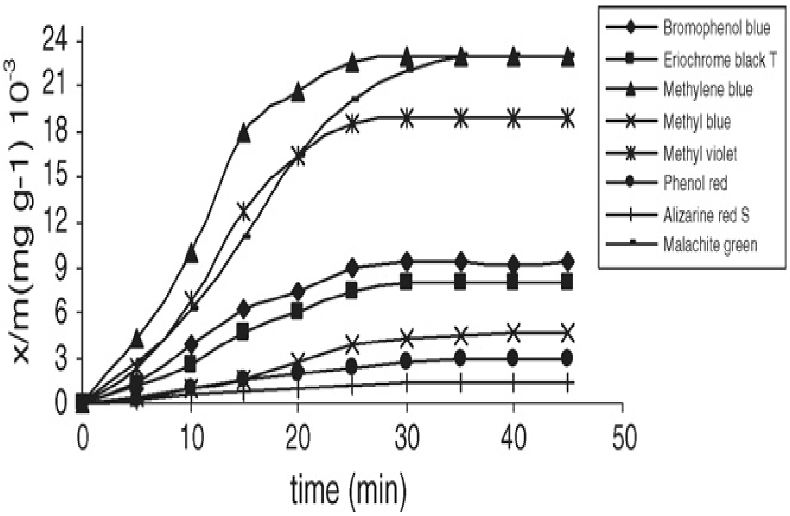

Fig. 2.2 Plot of shaking time vs. amount adsorbed on activate charcoal for various dye solutions

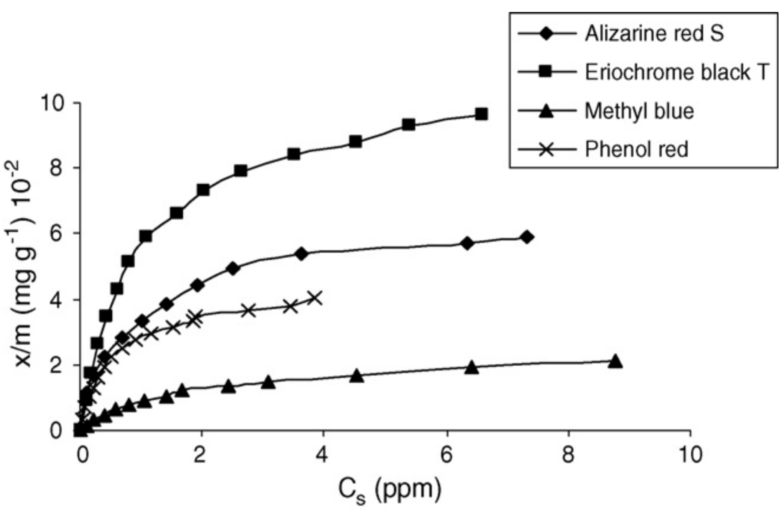

Fig. 2.3 Adsorption isotherm of various dyes on activated charcoal at 298 K

At temperatures of 298, 303, 308, 313 and 318, adsorption isotherms were obtained for bromophenol blue, alizarine red – S, malachite green, methylene blue, methyl blue, methyl violet, eriochrome black – T and phenol red. The results showed that charcoal had high affinity for adsorption; concluded from the L – type isotherms obtained.

Garg et al (2004) carried out the study of methylene blue removal using Indian rosewood sawdust, which is a timber industry waste. Indian rosewood or Dalbergia sissoo was washed with hot distilled water and after drying in sunlight till moisture removal, sieved in the range of 20 – 50 mesh ASTM. Colour and water-soluble substances immobilization was done using 1%

formaldehyde in the ratio of 1:5 (sawdust:formaldehyde, w/v) at 50°C for 4h. This was washed with distilled water for the removal of free formaldehyde and activated at 80 °C in a hot air oven for 24h. A part of this SD was then treated with sulphuric acid under certain conditions. Coconut shell was used as GAC or Commercially available activated carbon. The working volume was kept at 100mL of dye solution of known concentration.

Parameters such as pH, initial dye concentration, adsorbent mass were varied and later, adsorption dynamics was analyzed. It was found out that adsorption of methylene blue was dependent on adsorbent surface characteristics, adsorbent dose and methylene blue concentration in the wastewater. pH had very little effect on the adsorption. Adsorption kinetics was found to follow Lagergren first order kinetics model.

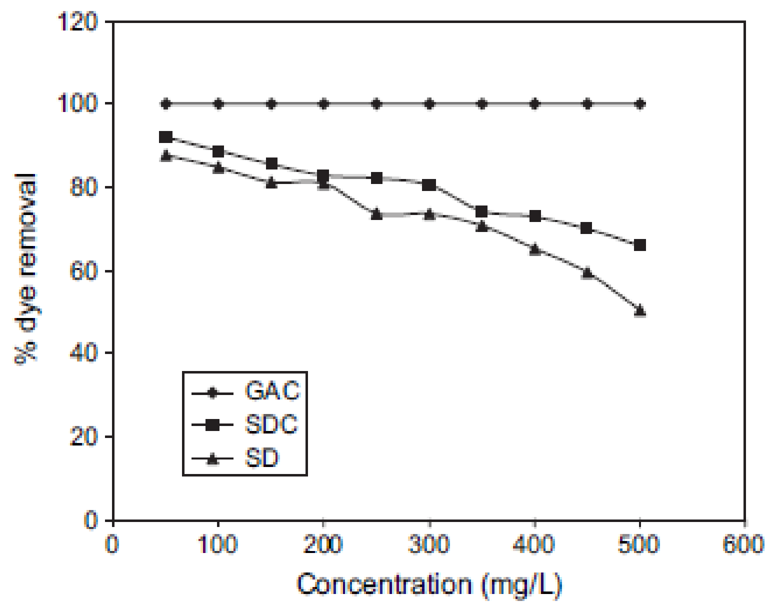

Fig. 2.4 Effect of adsorbent surface change on methylene blue adsorption (adsorbent dose = 0.4g/100mL)

Kansal et al (2007) carried out the study on photo degradation of two commercial dyes using different photocatalyst. Materials used for the experiment included Titania P-25 (surface area 50 m^2/g), SnO_2, CdS, ZnO, ZnS, Methyl Orange and rhodamine 6G. Irradiation experiments were carried on a 100mL dye solution after the addition of photocatalyst. The suspension was magnetically stirred throughout the experiment. At different time intervals a liquot was taken out using syringe and filtered through Millipore syringe filter of 0.45µm. absorption spectra was recorded and rate of decolorization was observed in terms of change in intensity at λmax of the dyes.

After comparison of Photocatalytic activity for different photocatalyst, it was established that ZnO is the most active one for decolorization of MO and R6G. Also, the activity was found to be greater in presence of sunlight than UV light. On increasing the initial dye concentration, rate of decolorization was found to decrease in case of each dye.

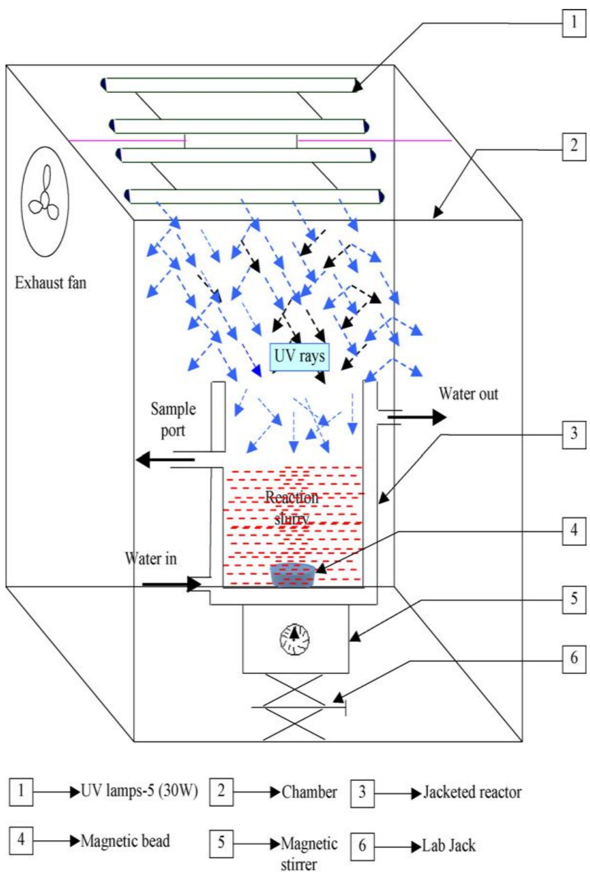

Fig. 2.5 Experimental setup for Photocatalytic process

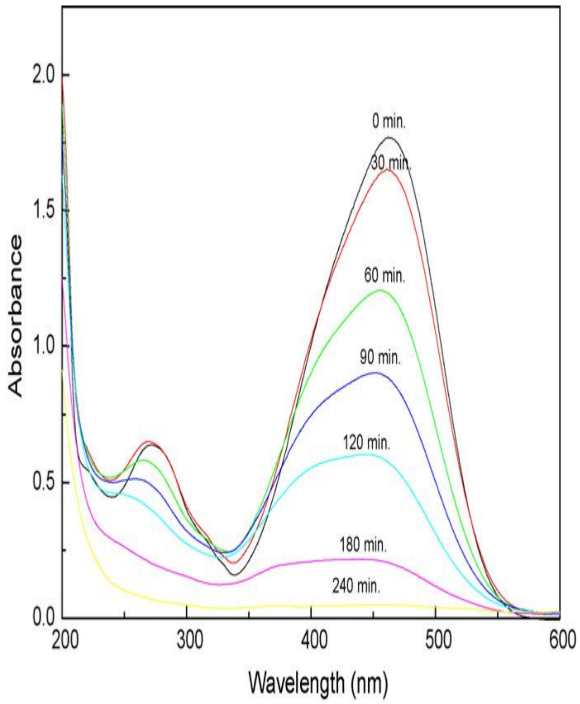

Fig. 2.6 Absorbance spectra of Methyl Orange during the course of reaction

Guibal et al (2007) carried out the coagulation and flocculation of dye – containing solutions using a biopolymer (Chitosan). Coagulation- flocculation experiments were carried out using Jar test equipment. The figure shows coagulation – flocculation of RB5 at pH 5 for initial different concentrations. Chitotsan concentration was varied for the determination of best dosage of coagulant for each dye concentration. Chitotsan dissolved in acetic acid was found to be very efficient for the coagulation – flocculation of Reactive Black 5. In acidic solution, charge neutralization was found to be responsible for the dye removal. When high molecular weight chitotsan was used, the process efficiency was found to decrease a bit because of reduced availability of amine groups.

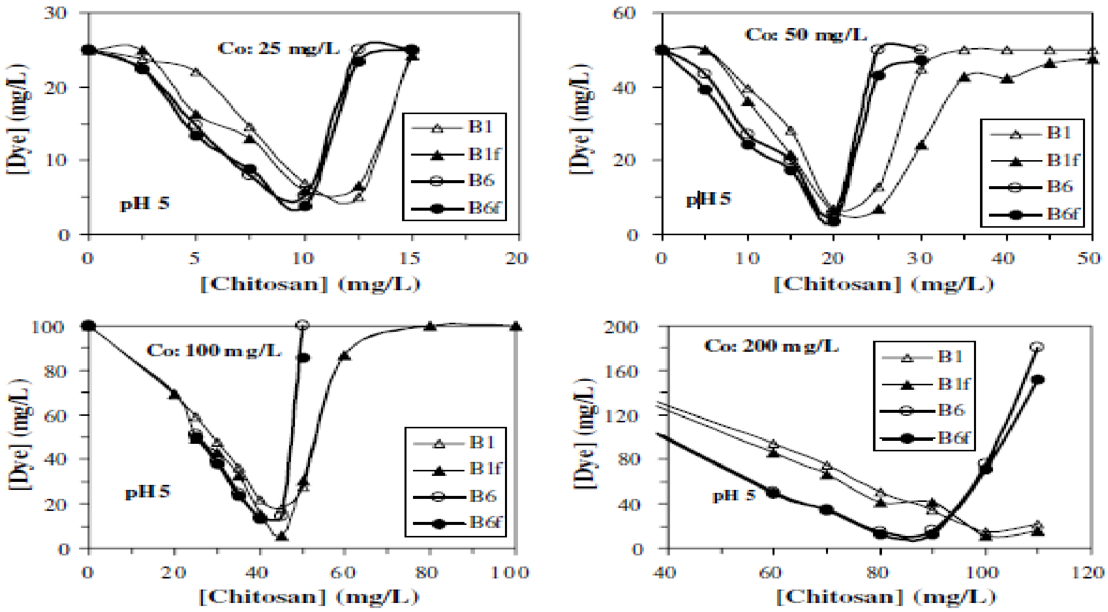

Fig. 2.7 Influence of filtration step on the optimum chitosan concentration for coagulation-flocculation of RB – 5at initial pH 5 (chitosans B1 and B6) at different initial concentration of dye.

Conley et al (1971) have carried out their work on adsorption studies related to kaolinite with the adsorption of amines. Adsorption studies were carried out at 25°C on a variety of kaoline samples. The kaolinites were converted to the hydrogen form just prior to adsorption experiments by elutriation with H_2SO_4 at pH3 (10 per cent solids) followed by water washing or the removal of traces of free acids and salts. This sample was further dried for about 16 hr. Rheological specimens were prepared using a Waring blendor and dispersion viscosities were determined with a model RVF Brookfield viscosimeter. Adsorption isotherms were obtained with five solution concentrations within the Langmuir region, from about 400µM to 1800 µM. the results showed that characteristically, strong amines follow a particle size dependent adsorption process as shown in Fig. 2.7.

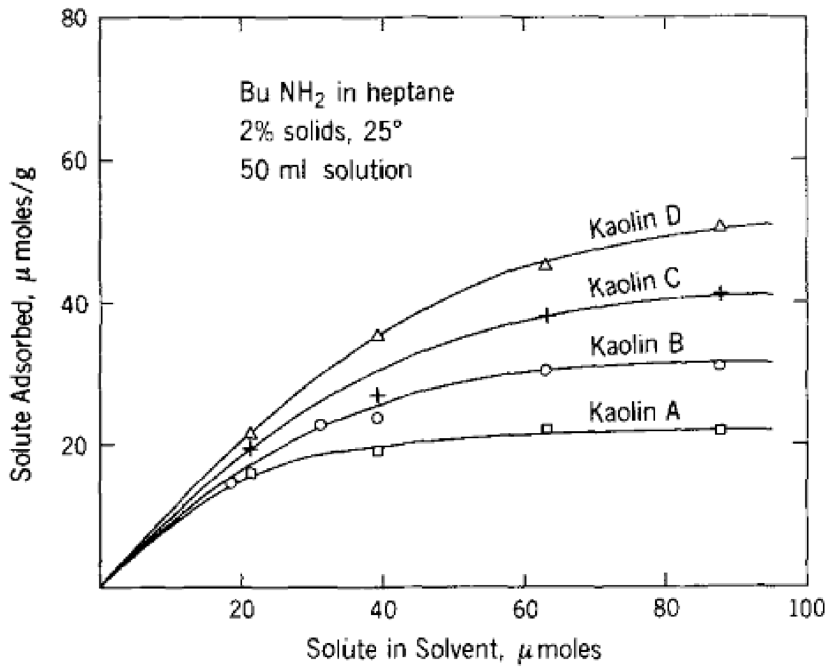

Fig. 2.8 Langmuir adsorption isotherms for kaolinite samples

2.3 Concluding Remark

Much of the work has been done in the field by making use of different adsorbents. They include activated charcoal, clay and other adsorbents. But, very little work has focused on increasing the adsorption efficiency of the adsorbent. In general, to achieve this enhancement, a different adsorbent is used or the amount of adsorbent is increased; either way makes the process very uneconomical. By making use of certain salts as additives, the adsorption capacity of the adsorbents can be greatly increased, and also, the process is very economical.

In the present project the effect of different salt addition on the adsorption capacity of clay has been studied. Kaolinite, a clay mineral, has also a broad variety of applications in the industry. It has low shrink – swell capacity, soft in nature and a low cation exchange capacity. It is mainly used in the paper industry and also to ensure the gloss on some grades of paper. It was also used by the US Naval Medical Research Institute as a kaolinite derived aluminosilicate nanoparticle.

Fig. 2.9 Kaolinite Structure

2.4 Research Objectives

In this project we have studied the effect of salt addition on adsorption capacity of kaolinite clay. Our main objective in this study is to investigate that to whether salt solution addition along with clay will enhance the adsorption capacity of the clay and to what extent. Also, we have tried to study what kind of changes the layers of clay undergoes after the salt addition.

2.5 Organization of the Thesis

In the thesis we have started with a brief introduction to the existing problem because of effluent discharge from dye industries. Then we have given some literature review and the basis and motivation of the project work. The materials and method section comes next where all the materials and their relevant properties have been specified in detail. The experimental methods adopted are explained clearly. The results and discussion part is done later and finally the conclusion of the project work.

Chapter 3

Experimental Procedure

3.1 Materials: Methylene Blue stain has been obtained from Merck Specialities Private Limited, Mumbai. Kaolinite clay was obtained from Loba Chemie Private Limited, India. Sodium Sulphate or Na_2SO_4 was purchased as RANKEM brand from Ranbaxy Fine Chemicals Limited. Sodium Chloride or NaCl was also purchased as RANKEM brand from Ranbaxy fine chemicals limited. Calcium chloride or $CaCl_2$ was purchased from Merck limited.

3.2 Methods: For all the experiments, a stalk solution of Methylene Blue (MB) of concentration 10mM was prepared. The working volume for the experiments was taken as 10mL. Depending on the desired concentration of the MB for the calibration plot, a measured volume of the dye solution was taken and diluted by adding distilled water. The solution was then shaken for about 30 minutes manually and then, transferred to centrifuge tubes of equal capacity as the working volume. Centrifugation was carried out at around 300rpm in a centrifuge for exactly 10 minutes. MB settled at the bottom leaving a dilute solvent floating on top. This solution or supernatant was then transferred to small tubes and absorbance measured was carried out. UV spectroscopy was used for the purpose. The obtained results were then plotted to obtain the graph.

For measuring the adsorption capacity of the kaolinite clay, 0.25g of the clay was fixed throughout the experiment. With the taken working volume, this measured clay was added and similar procedure as that of above was repeated.

For studying the adsorption enhancement of clay in presence of salts, three different salts of Na_2SO_4, NaCl and $CaCl_2$ with stalk solution concentration of 200mM, 500mM and 300mM respectively were prepared. Depending on the desired concentration of salt in the solution containing MB, clay and water, a measured concentration of the salt solution was taken and added to the whole solution. The remaining procedure and working volume remained same sa mentioned above.

Chapter 4

Results & Discussion

4.1 Calibration Plot

Experiments were carried to find out the relation between concentration and absorbance for Methylene Blue dye. 10mL solution of different known dye concentration were prepared and shaken and centrifuged as described in the Experimental section. The supernatant was separated and the absorbance was measured. Concentration range of dye was chosen so as to keep the absorbance value under 2. Ultraviolet (UV) Spectroscopy was used to find out the relation between concentration and absorbance. We found the relation between the two terms as y = 57.073x; where, 'y' is the absorbance and 'x' is the concentration. This relationship is essential as in all further experiments; we obtain absorbance value throughout, which needs to be converted to the concentration term.

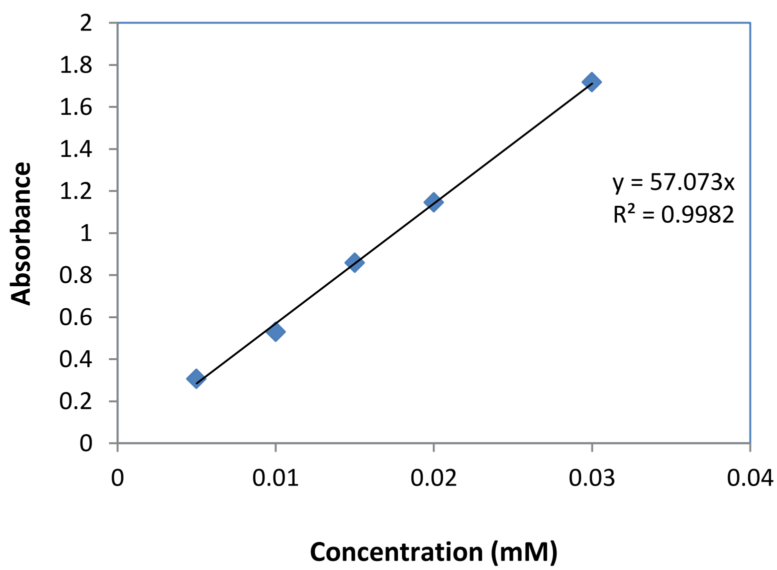

Fig. 4.1 Concentration Absorbance Plot

4.2 Adsorption Isotherm

This experiment is meant to determine the adsorption capacity of kaolinite clay. Throughout the experiment, we have kept the weight of kaolinite clay as 0.25g. We tried to find out that for this fixed sample of clay, what is weight of dye that could be removed so that, at the end of all experiments, we could compare the enhanced adsorption capacity of clay because of the presence of different salts. Dye samples of different known concentration (0.01mM – 1mM) were prepared where the working volume was kept at 10mL for each concentration of dye. To each sample, 0.25g of kaolinite clay was added and shaken as described in the experimental section. The obtained results were plotted as shown in the Fig. 4.2. It was observed that at around 0.3mM dye concentration, the clay adsorption capacity had reached its saturation level and no further adsorption was possible with the amount of clay we had considered.

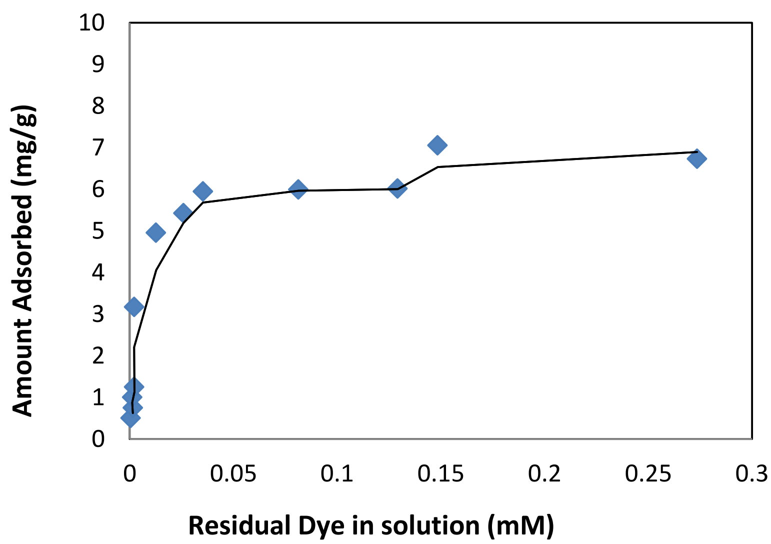

Fig. 4.2 Adsorption Isotherm for Kalolinite sample

4.3 Effect of electrolyte (Na_2SO_4) addition on the Adsorption process

After the determination of clay adsorption capacity, effect of electrolyte addition on adsorption efficiency of clay was studied. We started with Na_2SO_4 addition. Dye concentration was fixed throughout at 1mM and clay was kept constant at 0.25g. Electrolyte concentration was varied from 0 – 100 mM. Initially the variation was kept small to detect the saturation point for the electrolyte. Since, no saturation was achieved till 20mM, we increased the interval by 20mM till we reached the final concentration of salt in the working volume as 100mM. From the graph it was deduced that at around 40mM, the saturation was attained and no further dye removal was taking place beyond this point. Also, almost 100% adsorption enhancement took place after salt addition to dye and clay mixture. Dye adsorption went upto 0.6mM as compared to 0.3mM in the case of clay without any electrolyte.

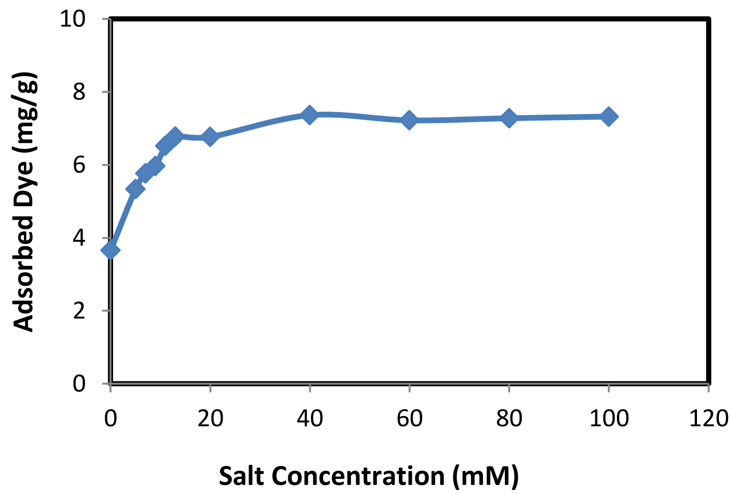

Fig. 4.3 Effect of Electrolyte (Na_2SO_4) on dye adsorption for a constant weight (0.25g) of clay

4.4 Effect of salt (NaCl) addition on Adsorption process

Similar study was carried out with another electrolyte, this time the salt solution being NaCl. Keeping the dye concentration fixed at 1mM and clay amount as 0.25g, the electrolyte concentration was varied in between 0 – 300mM. It was found out that at a concentration of 100mM of the electrolyte the adsorption capacity had reached at the saturation level and adsorption enhancement was about 93%.

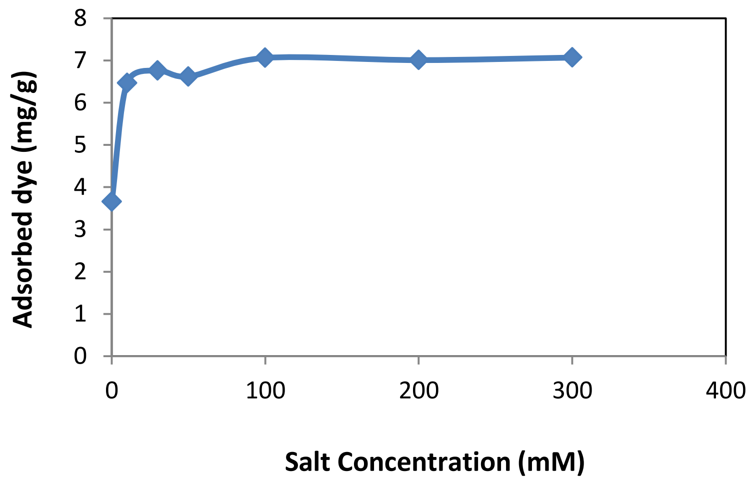

Fig. 4.4 Effect of Electrolyte (NaCl) on dye adsorption for a constant weight (0.25g) of clay

4.5 Effect of salt ($CaCl_2$) addition on Adsorption process

The same procedure was repeated with another salt solution of $CaCl_2$. Clay amount was fixed at 0.25g and the dye concentration was fixed at 1mM/L. At around 20mM of the electrolyte (Fig. 4.5), the saturation level of adsorption was achieved and the adsorption enhancement was about 67%.

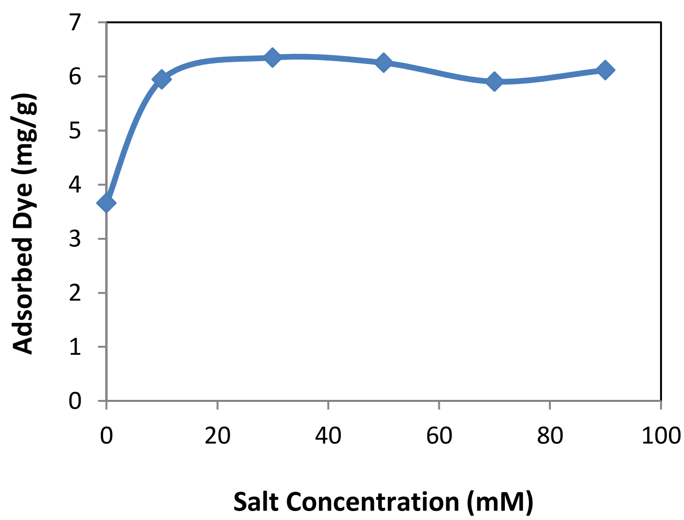

Fig. 4.5 Effect of Electrolyte ($CaCl_2$) on dye adsorption for a constant weight (0.25g) of clay

4.6 Study of FTIR spectra

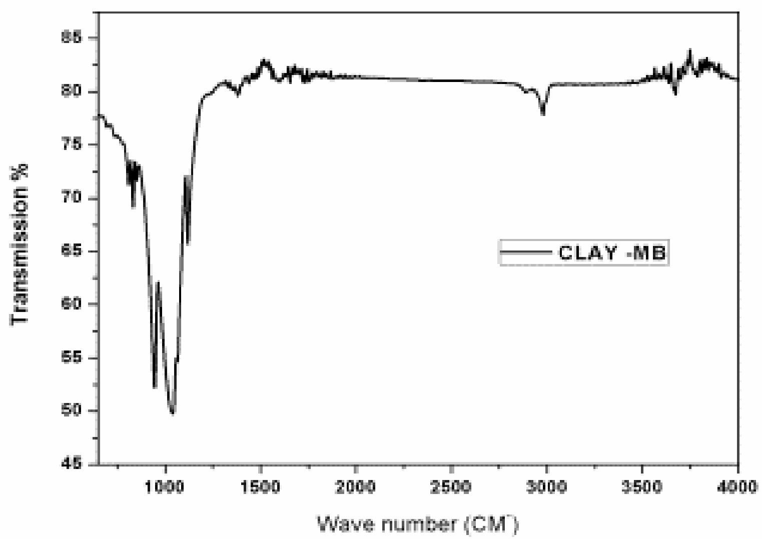

Fig. 4.6 FTIR spectra of Clay and Methylene Blue sample

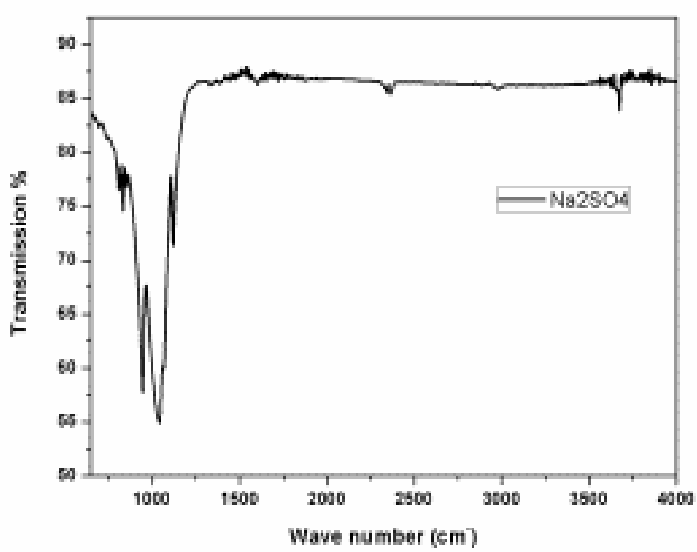

Fig. 4.7 FTIR spectra of Clay and Methylene Blue sample in presence of Na_2SO_4

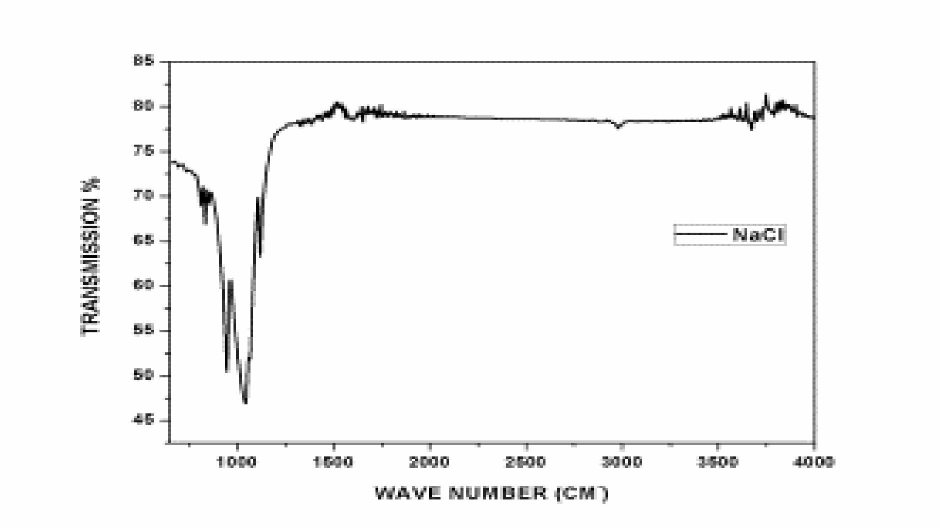

Fig. 4.8 FTIR spectra of Clay and Methylene Blue sample in presence of NaCl

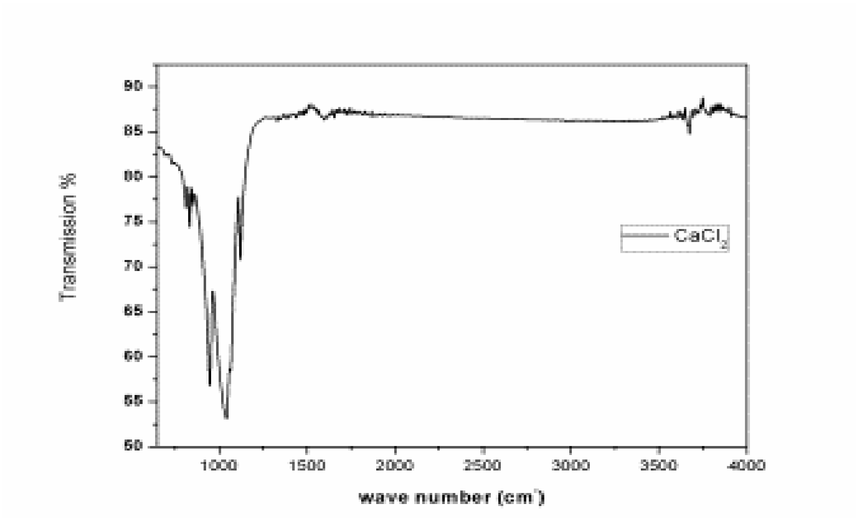

Fig. 4.9 FTIR spectra of Clay and Methylene Blue sample in presence of $CaCl_2$

Figure 4.10 shows the IR spectral patterns of pure kaolin (I), kaolin + methylene blue (II), and kaolin + methylene blue + electrolytes ($CaCl_2$ (III), Na2SO_4(IV), NaCl (V)).

From the spectrum (curve I) of the figure; peak at 942 cm^{-1} is for AlOH, peaks at 1029, 1054, 1117 cm^{-1} are due to SiO, and weak band at 3648 cm^{-1} corresponds to OH groups of the pure kaolin.

Kaolin exposed to methylene blue (curve II) and various electrolytes (curves III to V) exposed the major functional groups of kaolinite phase with peaks at 799 (due to SiOAl), 3696, 3667 cm^{-1} (due to OH groups)

Further peaks at 829 cm^{-1} for CH=C, and weak bands at 1364 cm^{-1} (due to $–CH_3$ symmetric deformation), and 1614 cm^{-1} (due to ring stretch) are for methylene blue which is associated with kaolin.

We can summarize that the kaolinite phase is a more ordered (with narrow and sharp peaks) after the electrolyte and methylene blue addition.

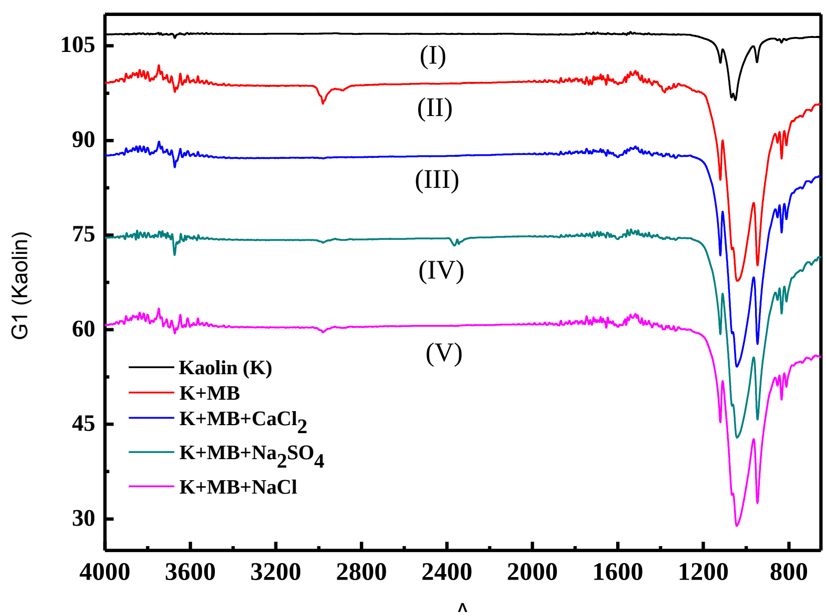

Fig. 4.10 FTIR spectra comparison (I) Kaoline (II) Kaoline +MB (III) Kaoline + MB + $CaCl_2$ (IV) Kaoline + MB + Na_2SO_4 (V) Kaoline + MB + NaCl

Chapter 5

Conclusion

Conclusion

The present study showed that Kaoline clay is a very effective adsorbent for the removal of methylene blue from the aqueous solution. The results showed that adsorption of methylene blue on clay were unaffected i.e. neither increased or decreased in presence of the surfactant (CTAB in this case). However, addition of salts of different valency had a marked effect on the adsorption capacity of the clay. For instance, addition of Na_2SO_4 increased the adsorption capacity by around 100%. The enhancement was, however limited to only a certain concentration of the particular salt solution addition, beyond which, there was no further adsorption enhancement. Thus, electrolytes alongwith Kaoline clay together, can serve as an excellent combination for carrying out of different dyes from Industries, thus solving the effluent discharge problems from these types of Industries.

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